

**SEASONAL TRANSPORT OF NITRATE  
INTO AND WITHIN A GROUND WATER AQUIFER  
QUALITY ASSURANCE AND QUALITY CONTROL  
FOR FIELD AND LABORATORY OPERATIONS**

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## QUALITY ASSURANCE PROJECT PLAN

Seasonal Transport of Nitrate Into and Within a Groundwater Aquifer

LDEQ Interagency Agreement No.

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### 3.0 PROJECT DESCRIPTION

The agricultural community is becoming aware of its role as a non-point source of surface and ground water pollution. By incorporating strategic management programs into the farming operation a responsible balance can be achieved between economic production and maintenance of a sound environment. The purpose of this research is to integrate the soil rhizosphere and the underlying ground water aquifer into a single system with respect to understanding the movement of nitrate originating as fertilizer amendments. Integration of the soil and aquifer environments should provide an awareness for improved management practices involving the timing of application of agricultural chemicals and the need for monitoring water quality in sensitive regions on a seasonal rather than annual basis.

The Mississippi River alluvial aquifer (MRAA) delineated in Figure 1, is the major source of water for the Tensas River Basin consisting of nine parishes in the northeastern corner of Louisiana. In 1984, 400 wells were active in public, industrial, and agricultural use, with an estimated 14,000 in use for rural domestic use (Louisiana Department of Transportation and Development Office of Public Works, 1984).

The presence of a high degree of interaction between the chemistry of the MRAA (shown in cross-section, Figure 2) and the chemistry of the overlying soil environment of the Macon Ridge has been demonstrated (Walthall et al., 1992a; 1992b). A band of saline ground water occurring in the MRAA beneath the Macon Ridge was found to be responsible for high levels of exchangeable sodium in the overlying soil. A similar relationship was observed for the distribution of chloride as well. While recognizing this undesirable soil condition to be of an uncontrollable, natural origin, it is the high degree of interaction between the soil environment and the underlying aquifer that is alarming. We hypothesize that if the aquifer can have such an extensive regional effect in supplying unwanted levels of sodium and especially chloride to these soils, in a similar manner, the soil environment may supply substantial levels of nitrate to the aquifer where salinity levels are low and do not restrict domestic usage.

A close examination of the data of Whitfield (1975) supports this hypothesis. Based on the upper depth of the screened interval of the wells sampled; 8 of 33 wells (24%) at depths of less than 50 feet had nitrate levels

greater than 10 mg/L, 4 of 73 (5%) exceeded this level at depths between 50 and 100 feet, and 1 of 21 (5%) wells exceeded this limit at depths greater than 100 feet. This concentration of nitrate in the upper portions of the MRAA strongly suggests that the contaminating source is being leached into the aquifer rather than being of an indigenous nature.

Guidelines in current use by the USDA Soil Conservation Service in Louisiana (Water Quality Handbook. II-3 Soil Rating for Nitrate and Soluble Nutrients) allow for the determination of nitrate leaching indices of specific soil types based on annual precipitation, hydrologic soil group, and rainfall distribution data. Three ratings are recognized in this system: high, intermediate, and nominal. The worst-case rating identifies situations in which nitrate movement below the root zone will occur and recommends either intense nutrient management or no application. All of the 13 soil series recognized on the Macon Ridge fall into this critical high rating (Martin et al., 1980; and Allen, 1993).

Our concern is for the potential contamination of the aquifer from excessive application of nitrogen fertilizers. A common argument is that nitrate levels are dispersed before reaching the depths at which wells are screened. In some cases this may be true. However, on the Macon Ridge the depth of domestic wells are often limited by the salinity of the ground water. Domestic wells are often elevated to avoid saline water that is encountered at greater depths in the aquifer. The environmental concern is that as domestic wells are elevated to avoid salinity there is a strong possibility of contacting nitrate contaminated waters at shallower depths.

The purpose of this work is to show that nitrate levels which exceed health standards for drinking water (10 mg/L nitrate-N) in a shallow ground water aquifer on the Macon Ridge in northeast Louisiana, are not random occurrences but can be predicted on a seasonal basis. Describing nitrate movement on a seasonal basis will be divided into two parts. **Objective 1** will focus specifically on transporting nitrate from the soil surface into the aquifer. **Objective 2** will describe dynamics within the aquifer which either concentrate nitrate at the top of the aquifer or disperse nitrate through lateral and/or vertical mixing.

We further propose to show that specific management practices can be used to effectively reduce nitrate levels over an annual cycle to meet health standards. **Objective 3** will demonstrate the effectiveness of specific management practices in

regulating factors or processes which determine the amount of nitrate leached.

### **Objective 1**

The strategy of this objective is to link soil and climatic factors which affect the mobility of nitrate to the variable concentrations of nitrate observed in the aquifer. The computer simulation model NLEAP (Nitrate Leaching and Economic Analysis Package), (Schafer, et al., 1991) will be used for modelling nitrate movement from the soil surface to the aquifer. The relevance of simulating the nitrate leaching process is to identify key factors or variables which can be manipulated by management practices to minimize nitrate leaching.

**Calibration** of the NLEAP model will be carried out during the early part of the study. A prerequisite for calibration of the model is that parameters necessary for model predictions be independently measured. It is planned to determine these parameters directly from soil measurements. If direct measurements are not experimentally feasible, estimates of such parameters specific to the soil series identified at our site will be used. This model contains regional soil and climate data bases containing data of specific soil properties for established soil series and local climate conditions. The soil data base consists of SCS soil characterization data of specific soil series.

Model input parameters include:

**Soil series** - The Gigger soil series is a very extensive soil type on the Macon Ridge and is recognized at our study site. The USDA-SCS taxonomic classification of the Gigger series is: fine-silty, mixed, thermic Typic Fragiudalf.

**Soil properties** - Two depth increments are recognized by the model for soil properties: 0 to 1 feet and 1 to 5 feet. Specific soil properties which will be determined for the Gigger soil at our site include: initial soil nitrate, organic carbon content, pH, CEC (exchangeable bases + exchangeable acidity). The model also requires definition of an initial nitrate value for the deep vadose zone (between a depth of 5 feet and the top of the aquifer). Soil properties to be used from the Gigger soil data base will include: bulk density, water holding capacity and soil water content at 15 bars.

**Climate** - In the case of precipitation, daily measurements are recorded at the Macon Ridge Branch Experiment Station and will be used for an event by event analysis. Temperature readings needed to drive evapotranspiration will be obtained



from the regional data base, using the St. Joseph climate data base, located approximately 40 miles east of our site.

Validation of the model for this phase of the study will address the amount of nitrate leached from the soil column (from the soil surface to the top of the aquifer). Linear regression will be used to examine how well predicted levels of nitrate leached by the model compare to actual nitrate levels observed in the soil column. The observed nitrate from soil columns will come from an existing data base collected over a three year period at the Macon Ridge Station in an adjacent field.

## Objective 2

While Objective 1 focuses on variables affecting nitrate movement over an annual cycle in the unsaturated zone (the soil column), **Objective 2** will focus on a different set of variables controlling movement within the aquifer. Some of these variables may follow an annual cycle and some may not. Two of the major variables we will attempt to characterize will be the variation in hydraulic conductivity and flow direction within the aquifer over an annual cycle. These variables are important because of their influence on lateral dispersion which could play a major role in reducing concentrated nitrate plumes entering the aquifer. Hydraulic conductivity will be determined using a pressure transducer to measure the response of the aquifer to addition or withdrawal of a known slug. Flow direction will be determined using an  $^{18}\text{O}$  enriched tracer.

Another variable which may affect aquifer dynamics at our site is the salinity gradient within the aquifer which results from the fresh water zone enriched with nitrate overlying a saline zone. While the approach will be somewhat empirical, it is critical to know the manner in which nitrate is dispersed either laterally or vertically. The NLEAP model recognizes an aquifer mixing zone varying in thickness from 1 to 10 feet and considers nitrate inputs as well as dilution from above and laterally. It is likely that simple dilution from leachate low in nitrate may account for reduction of elevated nitrate concentrations over an annual cycle, however, it is important to verify whether dispersion is actually confined to dilution in the 10-foot mixing volume. To address this question we will use an  $\delta^{18}\text{O}$  stable isotope tracer to determine the contribution of both lateral and vertical dispersion (Gonthier and Aharon, 1990). The  $\delta^{18}\text{O}$  isotope is harmless regarding human health and will not contaminate the aquifer. This stable isotope also offers the

advantage of not having to use a tracer such as bromide which can have density problems when introduced in high concentrations. Furthermore, this isotope has no adsorption characteristics common to some of the organic tracers in use. Monitoring wells have been configured such that a central 30-foot well will be spiked with the stable isotope, and the direction of flow detected either laterally by surrounding 30-, 40- and 50-foot wells located at a radius of 15 feet, or vertically by adjacent 40- and 50-foot wells. Sample collection for the tracer study will be on a scale of hours initially and reduced accordingly, dependent on conductivity.

### Objective 3

Two management practices will be evaluated for their effectiveness in regulating factors or processes which determine the amount of nitrate leached. The use of a split application of fertilizer will be tested for its ability to reduce the amount of nitrate available for leaching during the early part of the growing season. Preliminary work has shown that a critical time for leaching nitrate occurs between the time of planting and the establishment of the crop to the extent that evapotranspiration reduces effective leaching (usually the months of May and June). Approximately 45 kg/ha (50 lbs/ac) of urea ammonium nitrate (UAN) will be applied at the time of planting in early May with a similar amount applied in early July. In the second growing season of the study a single application of nitrate will be used.

The use of a winter cover crop of wheat will be tested for its effectiveness in immobilizing residual nitrate over the winter season when evapotranspiration is at a minimum (in a bare field) and leaching potential is at a maximum. The winter cover crop will follow the split fertilizer application treatment. The second winter season following the one-time fertilizer application will use no winter cover crop.

Sample collection frequency for monitoring nitrate over an annual cycle will vary. Samples for monitoring nitrate levels will be collected weekly during critical periods: the first month after fertilizer applications and the first month after defoliation. Sampling will be adjusted to bi-weekly and monthly intervals during periods in which little change is likely to occur.

Linear regression will be used to examine the accuracy of the NLEAP model at this final stage by comparing predicted aquifer nitrate levels to observed nitrate levels in monitoring wells. The results of the  $\delta^{18}\text{O}$  isotope tracer investigation will

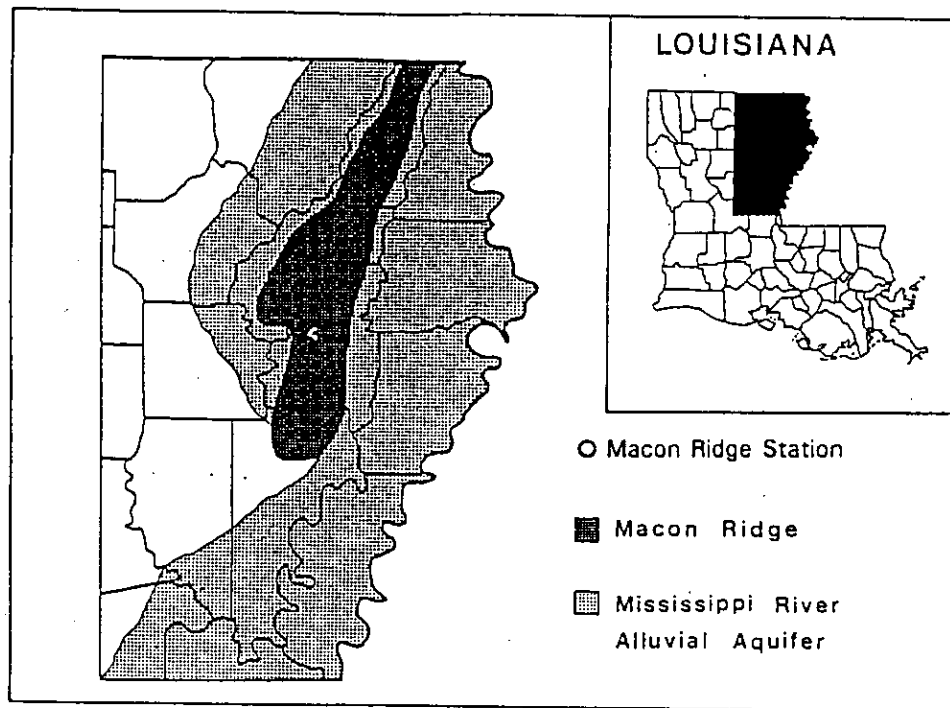


Figure 1. Delineation of the Mississippi River alluvial aquifer as it underlies the Macon Ridge in northeast Louisiana.

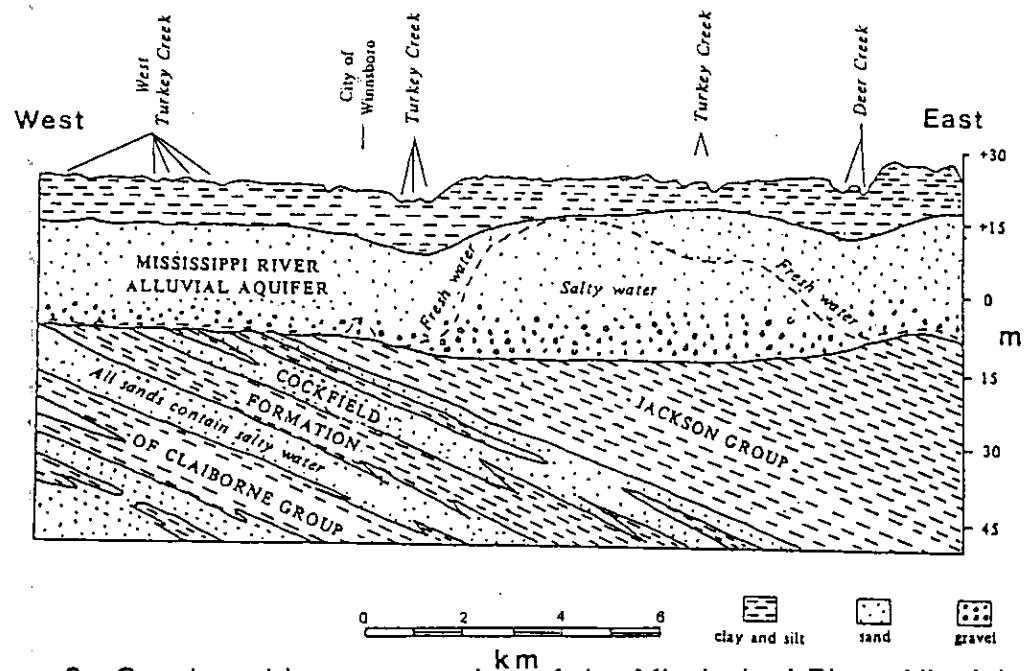


Figure 2. Stratigraphic cross-section of the Mississippi River Alluvial Aquifer near the city of Winnsboro, Louisiana. The Macon Ridge Research Station is approximately one-half mile south of Winnsboro.

allow us to correct for the amount of lateral flow and any vertical dispersion effects otherwise not accounted for by the model.

#### Time-Line for Field Activities.

##### First Year

- January - Initiate bi-weekly sampling of monitoring wells.
- February - Continue bi-weekly sampling of monitoring wells.
- April - Submerge monitoring wells. Collect soil cores for determining initial soil parameters.
- May - Plant cotton, apply first half of fertilizer amendment (45 kg/ha).
- June - Cultivate, open monitoring wells, initiate weekly (at least 4 weeks) sampling of wells for nitrate.
- July - Apply second half of fertilizer amendment (45 kg/ha), continue weekly (at least 4 weeks) sampling of wells for nitrate.
- August - Reduce sampling intensity of wells for nitrate to bi-weekly.
- September - Apply defoliant, harvest, increase sampling intensity for nitrates to weekly (at least 4 weeks).
- October - Collect soil cores for determining nitrate content of soil and vadose zone. Plant winter cover crop, reduce sampling intensity of wells for nitrate to bi-weekly.
- November - Continue bi-weekly sampling of monitoring wells for nitrate.
- December - Continue bi-weekly sampling of monitoring wells for nitrate.

##### Second Year

- January - Continue bi-weekly sampling of monitoring wells for nitrate.
- February - Determine hydraulic conductivity. Initiate first  $\delta^{18}\text{O}$  spike test (sampling strategy will be determined from hydraulic conductivity measurement). Continue bi-weekly sampling of monitoring wells for nitrate.
- March - Continue bi-weekly sampling of monitoring wells for nitrate.
- April - Continue bi-weekly sampling of monitoring wells for nitrate. Submerge monitoring wells, disk winter cover crop. Collect soil cores for determining nitrate content of soil and vadose zone.
- May - Plant cotton, apply single fertilizer amendment (90 kg/ha).
- June - Cultivate, open monitoring wells, initiate weekly (at least 4 weeks) sampling of wells for nitrate.
- July - Reduce sampling intensity of wells for nitrate to bi-weekly.

- August - Determine hydraulic conductivity. Initiate second  $\delta^{18}\text{O}$  spike test. Continue bi-weekly sampling of monitoring wells for nitrate.
- September - Apply defoliant, harvest, increase sampling intensity for nitrates to weekly (at least 4 weeks).
- October - Collect soil cores for determining nitrate content of soil and vadose zone. Reduce sampling intensity of wells for nitrate to bi-weekly.
- November - Continue bi-weekly sampling of monitoring wells for nitrate.
- December - Continue bi-weekly sampling of monitoring wells for nitrate.

#### Third Year

- January - Continue bi-weekly sampling of monitoring wells for nitrate.
- February - Continue bi-weekly sampling of monitoring wells for nitrate.
- March - Final sampling of monitoring wells for this study.

#### Time-Line for Laboratory Activities.

##### First Year

(Nitrate analysis of well samples will be performed after each sampling event.

- January - Initiate calibration of NLEAP model.
- March - Quarterly Report
- April - Analyze soil samples for characterization of model parameters.
- June - Quarterly Report
- September - Quarterly Report
- November - Verification of nitrate leaching component of NLEAP using soil core data base.
- December - Annual Report.

##### Second Year

- January - Verification of aquifer response to use of split fertilizer application.
- February -  $\delta^{18}\text{O}$  isotope analysis from first spike test.
- March - Quarterly Report
- May - Verification of aquifer response to use of a winter cover crop.
- June - Quarterly Report
- August -  $\delta^{18}\text{O}$  isotope analysis from second spike test.

September - Quarterly Report  
December - Annual Report.

#### Third Year

January - Verification of aquifer response to use of single fertilizer application.  
March - Quarterly Report  
April - Laboratory analyses complete.  
May - Data compilation complete.  
June - Quarterly Report  
July - Verification of aquifer response to the absence of a winter cover crop.  
September - Quarterly Report  
October - Preparation of Final Report.  
December - Final Report.

#### Intended Use of Acquired Data.

The data acquired in this project will be used to demonstrate whether the management practices of using a split-application of fertilizer and a winter cover crop can effectively reduce excessive nitrate levels in ground water. The nitrate data base acquired from the monitoring wells will allow for verification of the NLEAP model. The  $\delta^{18}\text{O}$  data base will be used to identify any unexpected flow patterns in the aquifer that will need to be recognized if present. The purpose for this verification effort is to provide a calibrated management tool to producers of this region that is capable of evaluating a range of management schemes on crop yield and ground water quality.

#### 4.0 PROJECT ORGANIZATION AND RESPONSIBILITY

Key individuals responsible for ensuring the collection of valid measurement data and the routine assessment of measurement systems for precision and accuracy are summarized in Table 1. A chart depicting internal as well as external lines of authority of all parties involved in the project is presented in Figure 3.

Dr. Mark Walthall, Associate Professor in the LSU Agronomy Department, is the Principal Investigator and is responsible for overall management of the project.

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**Table 1. Personnel and responsibility for the project.**

| Personnel  | Responsibility  |
|--|---|
| Dr. P.M. Walthall<br>Associate Professor<br>Department of Agronomy<br>Louisiana Agricultural Exp. Stn. | Overall Project Leader<br>Well Maintenance, Sample Collection,<br>Laboratory Analyses, Computer<br>Analyses |
| Dr. E.P. Dunigan<br>Professor and Head<br>Department of Agronomy<br>Louisiana Agricultural Exp. Stn.   | Quality Assurance Officer   |
| Dr. R.L. Hutchinson<br>Professor<br>Macon Ridge Research Station<br>Louisiana Agricultural Exp. Stn.   | On-Site Management<br>Planting, Fertilizing, Cultivating<br>Harvesting                                      |
| Dr. Paul Aharon<br>Professor<br>Dept. of Geology and Geophysics<br>Louisiana State University          | Supervision of $\delta^{18}\text{O}$ isotope analysis   |
| Ms. Joanie Haigler<br>Research Associate<br>Department of Agronomy<br>Louisiana Agricultural Exp. Stn. | Exchangeable Base Cations - ICP   |
| Ms. Lois West<br>Research Associate<br>Department of Agronomy<br>Louisiana Agricultural Exp. Stn.      | Nitrate Analysis - Ion Chromatography   |
| Mr. Gary Goay<br>LDEQ - Office of Water Resources  | ES2<br>Nonpoint Source Section  |
| Ms. Jan Boydstun<br>LDEQ - Office of Water Resources   | Coordinator<br>Nonpoint Source Section  |
| Ms Emelise Cormier<br>LDEQ - Office of Water Resources   | Program Manager<br>Planning and Assessment  |

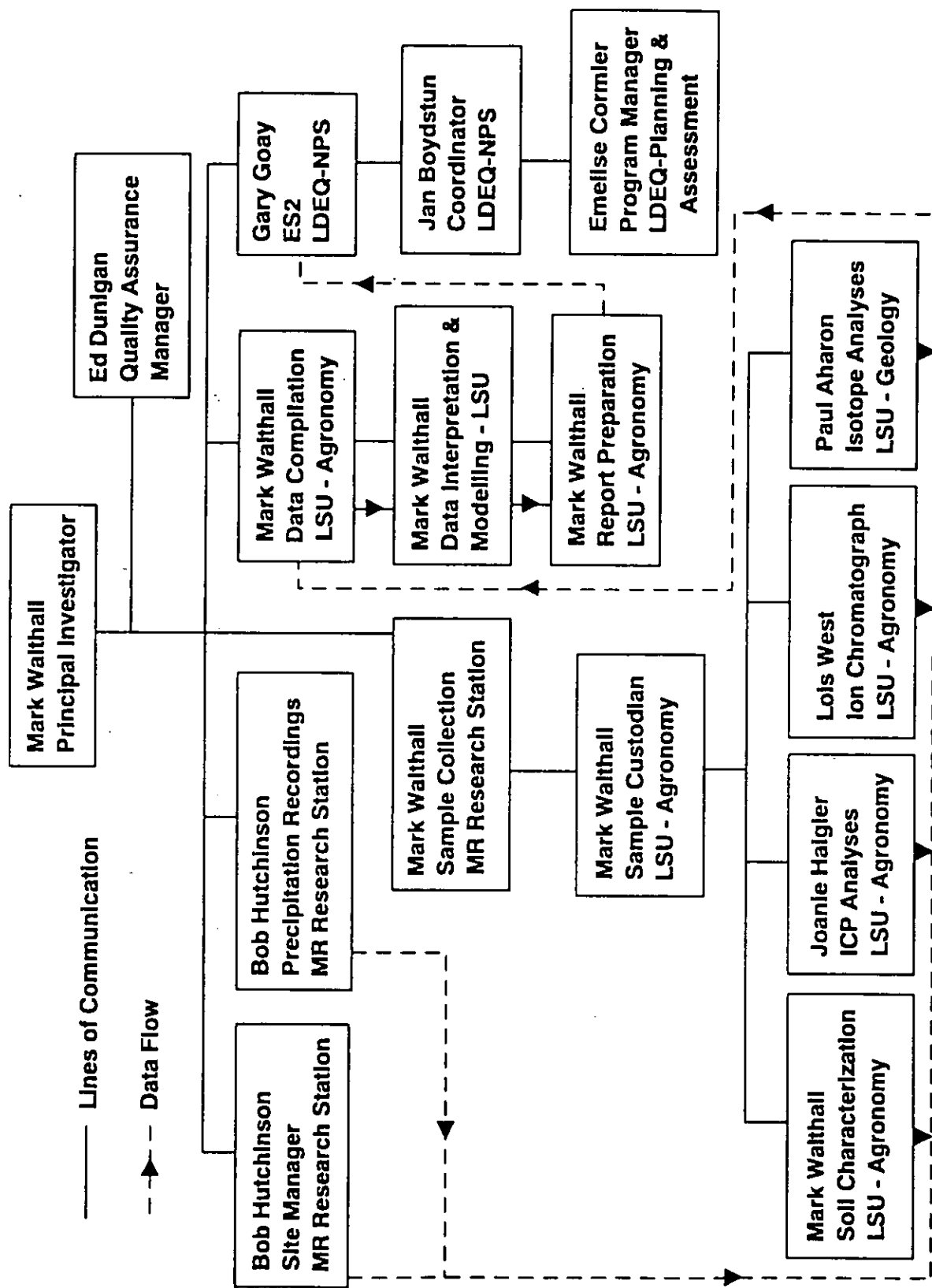


Figure 3. Project organization chart indicating lines of communication and data-flow pathway.



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He has 10 years of experience in the design, management, and operations of investigations. He will be in charge of sample collection and serve as sample custodian. All soil analyses (pH, OM, CEC, and water extractable  $\text{NO}_3$ ) will be performed in his laboratory in the LSU Agronomy Department. He will oversee data compilation, data interpretation, and modelling. He will also be responsible for the preparation of quarterly, annual and final reports.

Dr. Ed Dunigan, Professor and Head of the LSU Agronomy Department, will serve as the Quality Assurance Officer. He has 4 years experience as a professional chemist working for U.S. Rubber Company Polymer Research Laboratory and General Motors Research Laboratory and over 20 years experience working in the field of nitrogen fixation at LSU.

Dr. Bob Hutchinson, Professor and Director of the Northeast Research Station (which includes the Macon Ridge Branch Station) will serve as site manager in directing planting, fertilizing, conventional tillage operations, and harvesting at the Macon Ridge research site. He has over 15 years of experience managing the overall operation of a research station in which numerous researchers operate.

Dr. Paul Aharon is a Professor in the LSU Department of Geology and Geophysics. He is known internationally for his work in isotope geochemistry. In addition to conducting research in this field he teaches two graduate level courses specific to this project. Isotope Geochemistry - this course focuses on stable isotope fractionation in natural systems with emphasis on oxygen, hydrogen, and carbon isotope-ratio variation in natural waters. Mass Spectrometry for Isotope Geology - This course addresses the principles of thermal ionization mass spectrometry; chemical preparation of samples for isotope ratio measurements; and use of a multicollector solid source mass spectrometer.

Ms. Joanie Haigler, a Research Associate in the LSU Agronomy Department has a B.S. degree in Chemistry. She will be in charge of ICP analyses of soil extracts. She has over 8 years of experience and was trained in plasma atomic emission spectroscopy at the River Bend Nuclear Power Plant, St. Francisville, LA.

Ms. Lois West, a Research Associate in the LSU Agronomy Department has a B.S. degree in Agronomy from Colorado State University. She will be in charge of analyzing well samples for nitrate content. She has over 8 years of experience of operating a Dionex Ion Chromatograph. She was trained by the Dionex

Corporation Staff in operation of the LSU unit. She has participated in two additional Dionex workshops.

## **5.0 QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY**

Methodology used for the various chemical analyses is summarized in Table 2. The parameters have been discussed in **SECTION 3.0**.

Objective 1 - Describe the movement of nitrate from the soil surface into the aquifer.

Data for this objective will be used to define nitrate movement from the soil surface to the point where leachate enters the aquifer. This data will be interpreted using the nitrogen leaching model, NLEAP, which has the capability of identifying potential management practices capable of reducing the amount of nitrate available to leach. However, the model must be calibrated to the specific site conditions of the Macon Ridge before meaningful interpretation can be made. We will be comparing nitrogen leached (NL) predicted by the model to nitrate extracted from soil cores at a depth beginning below the root zone (5 feet) down to the aquifer sands (15 feet). A weighted average of each horizon or strata occurring within this depth zone will be summed for comparison to the NL predicted by the model. Monthly values of NL are computed by the model. Simulated values for months coinciding with dates at which cores were collected (bi-monthly) will be used in the calibration. This approach assumes that the amount of nitrate in the 5 to 15 foot zone will represent a monthly value of nitrate moving below the root zone. Agreement between actual and predicted NL will be assessed by regression analysis. Our goal is to obtain a p value of 5% to accept agreement between predicted and observed values of NL.

We will use archived soil-core samples collected from a three-year study. Soil cores were collected from test plots receiving annual amendments of 90 kg/ha ammonium nitrate. Water extracts from these cores will be analyzed for nitrate by an ion selective electrode. The detection limit for the nitrate electrode is approximately 0.1 mg/L nitrate-N. Replicate samples of water extracts from a

**Table 2. Method of analysis for chemical and physical parameters.**

| Parameter                                       | Method/<br>Instrumentation   | Detection Limit   |
|---|--|---|
| Nitrate   | Dionex Ion Chromatograph<br>EPA Method 200.7   | 0.05 mg/L   |
| $\delta^{18}\text{O}$                           | Mass Spectrometer  | 0.1 ppt vs. SMOW†   |
| Organic Carbon<br>in Soil                       | Wet oxidation - titration  | 1.0 g/kg  |
| Soil pH   | Orion specific ion electrode   | 0.1 (pH units)  |
| Exchangeable<br>Base Cations<br>(Ca, Mg, Na, K) | Ammonium Acetate Extract<br>(Thomas, 1982)<br>Inductively Coupled Plasma<br>Spectrometer - EPA Method<br>200.7 | Ca 0.005 mg/L<br>Mg 0.02 mg/L<br>Na 0.03 mg/L<br>K 0.2 mg/L |
| Exchangeable<br>Acidity                         | Potassium Chloride Extract<br>Titration with 0.1 N NaOH<br>(Thomas, 1982)                                      | 0.5 meq/100g soil   |
| Hydraulic<br>Conductivity                       | Heath (1989)   |   |

† Standard Mean Ocean Water

representative sub-set of the soil core samples varied less than 0.1 mg/L nitrate-N. Based on current work in our lab, both model output and soil extract data for NL range from 1 to 30 lb/ac of nitrate-N for monthly intervals. This represents a range of nitrate-N of 0 to 11 mg/L. A calibration range from 0 to 15 mg/L nitrate-N is used for the nitrate electrode. Analyses of extracts from the sample sub-set of soil-core samples by nitrate electrode were compared to analyses by ion chromatograph. The purpose of this test was to determine if there was potential interference of the nitrate electrode from chloride in the extracts. There was no observed interference for the range of chloride concentrations in this sample set. An  $r^2$  of 0.95 was obtained between the two methods used to determine nitrate.

Model input parameters to be determined for specific soil properties will include initial soil nitrate, organic carbon content, pH, and cation exchange capacity (CEC). Initial soil nitrate will be determined from replicated soil cores collected from the well site prior to fertilization and planting. This value is needed to define the initial nitrate status of the leaching field in the model. Nitrate will be determined on water extracts from each horizon or strata sampled with the same approach described above for the archived soil samples. Weighted averages will be determined for the upper one foot zone; the 1 to 5 foot zone; and the vadose zone (5 to 15 foot zone).

Organic carbon (OC) content is needed for computing inputs of nitrate from mineralization as well as losses due to microbial immobilization. The wet oxidation method to be used has a detection limit of 0.1% OC using a 0.5g sample. Based on previous analyses of a cultivated Gigger soil, we would expect a value between 0.75 and 1.25% OC. This method is reproducible within 0.1% OC. Replicate samples will be determined for each core sample falling within the 0 to 1 foot zone. A weighted average for the depth interval will be computed.

The soil pH is used to adjust the conversion rate of ammonium/ammonia lost in volatilization and will be determined in 0.01M  $\text{CaCl}_2$  (1:2, soil:solution) on replicate samples. This routine procedure has an accuracy of plus or minus 0.1 pH units. Values for pH are needed for the top one foot of the soil column. A weighted average for the depth interval will be computed.

The cation exchange capacity (CEC) is also involved in determining the amount of nitrogen lost to volatilization. The sum of cations method for determining CEC is recognized to be accurate to within 0.5 meq/100g soil with a

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detection limit of 0.5 meq/100g as well. Replicate samples will be determined for each core sample falling within the 0 to 1 foot zone. Expected values should range from 5 to 15 meq/100g soil.

Objective 2 - Describe aquifer dynamics which either concentrate nitrate at the top of the aquifer or disperse nitrate through lateral and/or vertical mixing.

The purpose of this objective is to determine how the hydrology of the aquifer responds to the introduction of soil leachate containing seasonally elevated levels of nitrate. Previous work from our study site has shown that nitrate levels exceed established limits for drinking water sporadically throughout the year in the shallow reaches of the aquifer. The effects of dilution and dispersion on the concentration of nitrate leached as it enters the saturated conditions of the aquifer are a major concern. In order to calibrate the NLEAP model to the aquifer conditions beneath the Macon Ridge several parameters must be defined. These include the hydraulic conductivity and the lateral versus vertical flow components in the aquifer mixing zone.

The Mississippi River alluvial aquifer at the depth range of interest for our site consists of coarse sands. During the course of previous samplings several observations into the rate of recharge within the aquifer were made. Wells were sampled and purged and could not be bailed dry by use of a downwell pump. On February 2, 1995 an initial water level reading was taken, the wells pumped for approximately 5 minutes, sampled, and the water level remeasured. Complete recharge took place in the short time between pulling the pump out of the well and remeasuring the water level. Personal conversations with geologists from the U.S.G.S. have confirmed the difficulty in making conductivity measurements based on their own work in the area. Because of high conductivity, pumping rates would have to be higher than our present capabilities to allow for a significant drawdown (pumping test). A slug test is also out of the question due to the unrealistic size of a slug necessary to cause a measurable displacement within such a large aquifer.

The hydraulic conductivity will be determined using a pneumatic slug test. Air will be inserted into an existing well with an air compressor. A pressure transducer (PXD-260) will be inside the well to measure drops in aquifer levels. Water levels will be recorded by a HERMIT 1000C data logger. The well will be purged by air to a depth of 6 feet below the top of the screen. The air pressure will then be released so the aquifer can recharge back to its original head level.

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The transducer will record changes in water elevation on 0.2 second intervals for the first 20 seconds, 1 second for the next 20-60 seconds, and 12 seconds for the next ten minutes. Hydraulic conductivity tests will be repeated three times for each well, for each of the screened intervals (30, 40, and 50 feet). Results will be downloaded and aquifer water levels will be plotted against time. Conductivity will then be determined by the Hvorslev Method (Hvorslev, 1951).

Instrumentation consists of a data logger and a pressure transducer. The pressure transducer is a PXD-260 model (factory calibrated). The polyurethane and teflon lead cable is vented to the atmosphere to allow the transducer to compensate for fluctuations in barometric pressure. Transduction is measured from an integrated silicon strain gauge bridge that moves with changes in water level. The resolution of transducer measurements falls within  $\pm 0.16\%$  of the range being measured if there are no temperature fluctuations greater than  $20^{\circ}\text{C}$ . For example, a 30 foot reading would have an accuracy range varying no more than  $\pm 0.048$  feet (30 feet  $\times$  .0016). The data logger we plan to use is a HERMIT 1000C with a 32K non volatile memory and 20-self diagnostic checks. Data can be transferred via RS232C port to a personal computer for analysis without interrupting data collection. Sampling schedules can be preprogrammed with logarithmic sampling rates and 16,000 data point capacity. Resolution of measurements for the data logger falls within  $\pm 0.06\%$  of measured range at constant temperature, and  $\pm 0.2\%$  of measured range with temperature fluctuations. Stability of data logger measurements is  $\pm 0.002\%$  of range being measured.

An additional parameter that will be addressed regarding calibration of the NLEAP model is the extent of lateral flow occurring in the mixing zone of the aquifer for which nitrate concentrations are calculated. If there is no lateral flow, the model takes the monthly value of NL and distributes it through the volume of the mixing zone. In the case of leachate high in nitrate, an increase in aquifer nitrate is observed. When nitrate is essentially zero in leachate, a drop due to dilution in preexisting nitrate level occurs.

The purpose of the  $\delta^{18}\text{O}$  study is to characterize the lateral and vertical flow components of the aquifer mixing zone. The strategy of this study will be similar to the pneumatic slug test in that an  $^{18}\text{O}$  enriched spike will be released from the center-30 foot well. Samples will then be collected from all surrounding wells at specific time intervals (hourly at first increasing to approximately 12 hours before

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termination of the test. In addition to obtaining a second independent hydraulic conductivity we will also have flow direction for lateral flow.

The  $^{18}\text{O}/^{16}\text{O}$  ratios will be determined by mass spectrometer (Gonthier and Aharon, 1990) and reported in the conventional delta ( $\delta$ ) notation relative to V SMOW standard,

$$\delta(\text{‰}) = [(R_s/R_r) - 1] \times 1000$$

where  $R_s$  and  $R_r$  are the  $^{18}\text{O}/^{16}\text{O}$  in the sample and reference standard. Repeats of the laboratory reference standard give a precision of  $+0.1\text{‰}$  (Gonthier and Aharon, 1990).

In a recent investigation Dr. Aharon (personal communication) spiked a well with 5 ampules of a 100 ml tracer having a concentration of 1.5 Atom %  $^{18}\text{O}$ . Atom %  $^{18}\text{O}$  is related to  $\delta^{18}\text{O}$  by the following relationship:

$$\text{Atom \% } ^{18}\text{O} = 0.20052 \left( \frac{\delta^{18}\text{O}}{1000} + 1 \right)$$

A  $\delta^{18}\text{O}$  value of  $+37,000$  was measured in the spiked well. A  $\delta^{18}\text{O}$  value of  $+1.4$  was determined in a monitoring well at a lateral distance of 100 feet. This is in contrast to a  $\delta^{18}\text{O}$  value for ground water of  $-3.0$ . The maximum lateral distance the spike will travel in our well design is approximately 20 feet. The maximum vertical distance would be 30 feet. Given these well constraints and the analytical precision of the  $\delta^{18}\text{O}$  determination, our approach should be quite feasible.

**Objective 3 - Evaluate the effectiveness of specific management practices in regulating the amount of nitrate leached.**

The purpose of objectives one and two is to provide a management tool for simulating nitrate leaching, that accurately reflects the soil and aquifer environments of the Macon Ridge. The purpose of objective three is two-fold. First we want to determine the effectiveness of two management practices believed to have a high potential for reducing the amount of nitrate available to leach (the use of a winter cover-crop and the use of a split-application of nitrate fertilizer). Second we want to validate whether the calibrated NLEAP model can

accurately predict alterations in management schemes on nitrate levels within the aquifer.

Nitrate concentrations in samples pumped from the monitoring wells will be used in evaluating both phases of this objective. The effectiveness of the split-application fertilizer treatment will be evaluated by contrasting nitrate concentrations in wells to a one-time fertilizer application treatment. The same approach will be used in characterizing the ability of a winter cover-crop to immobilize nitrate by comparing well data to a treatment in which no cover-crop is used.

Nitrates in well samples will be analyzed by ion chromatograph (IC). We use a working detection limit of 0.5 mg/L nitrate (0.1 mg/L nitrate-N). Precision for replicate samples is within + or - 0.05 mg/L nitrate (0.01 mg/L nitrate-N). The data will need to indicate whether excessive levels of nitrate (> 10 mg/L nitrate-N) can be substantially reduced to near background concentrations (lowest levels observed in monitoring wells throughout the year) of < 2 mg/L nitrate-N in the wells screened between 20 and 30 feet. These goals should be realized given the analytical range and precision of the IC.

Validation of simulated nitrate concentrations in the aquifer mixing zone to observed values from the wells will be carried out using the same approach described for the NL parameter for the vadose zone. Agreement between actual and predicted nitrate concentrations will be assessed by regression analysis. Our goal is again to obtain a p value of 5% to accept agreement between predicted and observed values of nitrate in the aquifer.

## 6.0 SAMPLING PROCEDURES

Sample collection will address three major tasks: (1) soil samples for calibrating the NLEAP model, (2) ground water samples for verifying nitrate leaching estimates from NLEAP, and (3) ground water samples for determining hydraulic conductivity and flow direction in the aquifer ( $\delta^{18}\text{O}$  isotope study). Sampling procedures will follow the recommendations in *Standard Methods* (APHA, 1989) where applicable. The study site from which all soil and well samples will be collected is located on the Macon Ridge Research Station, approximately one-half mile south of Winnsboro, Louisiana (latitude 32° 08' 02", longitude 91° 41' 41"). A detailed sampling schedule is presented in Section 3.0.



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**Soil Samples** will be collected using a Gidding's hydraulic probe. Cores, 2 inches in diameter, will be collected to characterize three depth zones recognized by the NLEAP model: 0 to 1 feet, 1 to 5 feet, and a deep vadose zone which will extend from 5 feet to the beginning of coarse aquifer sands, approximately 15 feet. Duplicate cores will be collected. Soil samples will be sealed in plastic zip-lock bags for transport to the laboratory. Upon arrival to the laboratory at LSU, samples will be air-dried, ground if necessary to pass through a 2-mm sieve and stored until time of analyses.

**Water Samples** for both nitrate and isotope analyses will be collected using a Grundfos Redi-Flo2 portable, submersible pump. Each monitoring well will be purged of three well volumes as per USGS guidelines. Samples will be collected in acid-washed polyethylene bottles. Nitrate samples will be stored in ice chests during transport to the laboratory and refrigerated at 4° C prior to being analyzed. Samples will be scheduled for nitrate analysis within 48 hours of reaching the laboratory.

Isotope samples will be transported to the laboratory under ambient conditions, sealed with parafilm and stored at room temperature in closed cabinets until time of analysis. These special precautions are to minimize any evaporation loss which would preferentially concentrate the heavier  $^{18}\text{O}$  isotope relative to the lighter  $^{16}\text{O}$  isotope. The ratio of these two isotopes is the critical factor in this analysis. For this reason special precautions are taken to seal the samples (parafilm seal in addition to bottle cap) and reduce any desiccation (refrigeration). The  $\delta^{18}\text{O}$  for the ground water is expected to fall within a very narrow range and effectively fingerprint the aquifer. The intent of the  $^{18}\text{O}$  enriched spike is to alter the ratio of the ground water such that hydraulic conductivity and flow direction can be characterized by the shift in the isotope ratio as the spike moves into the surrounding monitoring wells.

## **7.0 SAMPLE CUSTODY**

**Sample Custodian** - Sample custody will be the responsibility of the Principal Investigator, Mark Walthall of the LSU Agronomy Department. A hard copy of all data will be kept on file in addition to being stored on floppy disks in the office of the Sample Custodian.

**Field Operations** - Water samples will be labeled with time, date, well number, and whether they are nitrate or  $\delta^{18}\text{O}$  isotope samples (Figure 4). Soil samples will be labeled with date and depth increment sampled from. Both soil and water samples will be logged into a field notebook at time of collection (Figure 5). Samples will be transported from the Macon Ridge Research Station to the LSU Agronomy Department on the day of sample collection for nitrates. Samples collected for the  $\delta^{18}\text{O}$  tracer study will be collected over a 2 to 3 day period before transport to the laboratory because of sampling intensity. Samples will be stored under ambient conditions in sealed storage chests to minimize air flow and desiccation.

**Laboratory Operations** - Upon delivery to the LSU Agronomy Department, all samples will be logged into a laboratory notebook and double checked against the field notebook. Laboratory personnel will sign and date the log book to document arrival of samples (Figure 6). Samples for isotope analyses will then transported to Dr. Aharon's laboratory in the LSU Geology Department, logged into a laboratory notebook (Figure 6), and double checked with the master inventory list.

All soil analyses and nitrate analyses on well samples will be performed in the LSU Agronomy Department. The  $\delta^{18}\text{O}$  samples will be analyzed in the LSU Geology Department.

When a sample is analyzed, the sample number and type of analysis will be recorded in the log book. A hard copy printout of all analyses will be kept on file. Data will be stored on computer disks for analysis.

## **8.0 CALIBRATION PROCEDURES AND FREQUENCY**

**Field Equipment** - All field equipment involved in data acquisition is either factory calibrated or requires no on-site calibration.

**Laboratory Equipment** - Table 3 lists the calibration procedures, frequencies, and tolerances for the equipment used for analyses of the proposed parameters. Calibration procedures will be conducted according to manufacturer's specifications.

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## Macon Ridge Nitrate Leaching Study

Sample Type:            Nitrates            Isotopes

Sample Number: \_\_\_\_\_ (Well No.) - \_\_\_\_\_ (Date)

Time: \_\_\_\_\_

Sampled By: \_\_\_\_\_

Figure 4. Example of Sample Label for Well Samples.

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| Macon Ridge Nitrate Leaching Study<br>Field Tracking Report |                   | Page _____ |      |         |
|---|-------------------|------------|------|---------|
| Field Sample Code   | Brief Description | Date       | Time | Sampler |
|   |                   |            |      |         |
|   |                   |            |      |         |
|   |                   |            |      |         |
|   |                   |            |      |         |
|   |                   |            |      |         |
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|   |                   |            |      |         |
|   |                   |            |      |         |

Figure 5. Sample of Field Tracking Report Form to be kept in Field Log Book.

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Figure 6. Sample of Chain of Custody Record in Laboratory Sample Log Book.

## 9.0 ANALYTICAL PROCEDURES

**Ion Chromatography Analysis** - The LSU Agronomy Department has a Dionex ion chromatograph. All well samples collected for nitrate analysis will be analyzed by ion chromatography. Replicate analyses will be made on 25% of all samples within each batch (approximately 6 out of 24 samples). Any samples falling outside of the calibration range for the instrument will be diluted to within the calibrated range and reanalyzed. Instrumental drift is checked every 10 samples. If drift exceeds 5% the instrument is recalibrated and the previous 10 samples reanalyzed. An internal QA/QC sample independent of calibration standards, is included in each batch of analyses. If the QA/QC value varies more than 5% from the accepted value, the batch will be reanalyzed.

**Water extractable soil nitrate** - Water extracts from soil core samples (1:5, soil:water) will be analyzed for nitrate by an ion selective electrode. The detection limit for the nitrate electrode is approximately 0.1 mg/L nitrate-N. Replicate samples of water extracts will be analyzed. A calibration range of 0 to 15 mg/L nitrate-N should be appropriate based on past experience. If necessary samples will be diluted so that they fall within the calibration range. Instrumental drift will be monitored every 5 samples using high and low calibration standards. If instrumental drift exceeds 0.1 mg/L nitrate-N, the unit will be recalibrated and the previous 5 samples reanalyzed. An internal audit sample will be included with each batch of samples. If this sample varies by more than 0.1 mg/L nitrate-N, the batch will be reanalyzed.

**Isotope analysis** - Ratios of  $^{18}\text{O}/^{16}\text{O}$  will be made on a gas-source mass spectrometer located in the LSU Geology Department following the methodology of Epstein and Mayeda (1953). Isotope ratios of samples are compared to a Standard Mean Ocean Water (SMOW) standard. Laboratory analyses indicate a precision of 0.1‰ for  $\delta^{18}\text{O}$  using the SMOW standard.

The following analyses are for a one time characterization of the 0 to 1 foot depth zone. To our knowledge, there is no NBS soil standard for these parameters. An internal audit sample will be utilized as described.

**Organic carbon** - The wet oxidation method using chromic acid an oxidizing agent followed by back titration with ferrous ammonium sulfate has a detection

**Table 3. Calibration and tolerance of laboratory instruments.**

| Instrument         | Calibration and Tolerance |                                |
|--------------------|---------------------------|--------------------------------|
|                    | Time                      | Specifications                 |
| IC                 | Upon Use                  | NO <sub>3</sub> 0.2 to 40 mg/L |
| ICP                | Upon Use                  | Ca 0 to 250 mg/L               |
|                    |                           | Mg 0 to 250 mg/L               |
|                    |                           | Na 0 to 250 mg/L               |
|                    |                           | K 0 to 100 mg/L                |
| Mass Spectrometer  | Upon Use                  | -54 to -1 ppt vs. SMOW†        |
| pH Meter           | Upon Use                  | Buffers 4.0/7.0                |
| Analytical Balance | Monthly                   | 0.1 mg                         |

† Standard Mean Ocean Water

limit of 0.1% OC using a 0.5g sample. The method is reproducible within 0.1% OC. Replicate samples will be analyzed. If an internal audit sample varies by more than 5% of the accepted OC value, the batch will be reanalyzed.

**Soil pH** - Soil pH will be determined in 0.01M CaCl<sub>2</sub> on replicate samples. This routine procedure has an accuracy of + or - 0.1 pH units. Instrumental drift will be monitored every 10 samples using high and low calibration standards. If instrumental drift exceeds 0.1 pH units, the unit will be recalibrated and the previous 10 samples reanalyzed. An internal audit sample will be included with each batch of samples. If this sample varies by more than 0.1 pH units, the batch will be reanalyzed.

**Cation exchange capacity** - The CEC will be determined using the sum of cations method in which exchangeable bases are extracted using a 1M solution of ammonium acetate and exchangeable acidity extracted with a solution of 1M potassium chloride. Exchangeable bases are determined by ICP. Extractable acidity is determined by titration. The precision of this method is within 0.5 meq/100g. An internal audit sample will be included with each batch of samples. If this sample varies by more than 5% of the accepted value, the batch will be reanalyzed.

**ICP Analysis** - The LSU Agronomy Department has an ARL 34,000 ICP dedicated for research. Standards will be matrix matched to samples (1M ammonium acetate). Any samples falling outside of the calibration range for the instrument will be diluted to within the calibrated range and reanalyzed. Instrumental drift is checked every 10 samples. If drift exceeds 5% the instrument is recalibrated and the previous 10 samples reanalyzed. An internal QA/QC sample independent of calibration standards, is included in each batch of analyses. If the QA/QC value varies more than 5% from the accepted value, the batch will be reanalyzed.

It is the responsibility of the specific instrument analyst to identify instrument drift failure and reanalyze affected samples. It is the responsibility of the person in charge of data compilation, Mark Walthall, to identify any failure in analytical operations associated with internal QA/QC samples and batch samples and to direct reanalysis of affected samples.



## 10.0 DATA REDUCTION, VALIDATION AND REPORTING

The lab analyst will perform the calculations and calibrations to quantify the concentration of a specific parameter. The data will then be transferred to a final data sheet and submitted to the project leader. Verification of calculations and transcriptions will be made by the project leader.

## 11.0 QUALITY CONTROL REQUIREMENTS

### Field

All equipment will be maintained in a clean and operable condition. An additional submersible pump is requested in this proposal to serve as a back-up to the system currently in use. A back-up electric generator is available at the Macon Ridge Station.

All wells are pumped of three well volumes before any samples are collected as per USGS guidelines. All wells are carefully sealed when not being sampled to prevent well contamination. Soil and water samples will be logged into a field notebook at time of collection.

All water samples will be collected in acid-washed polyethylene bottles.

### Laboratory

Appropriate calibration standards for IC, ICP, and specific ion electrodes (pH, nitrate) will be developed from certified stock solutions.

An internal QA/QC sample used in IC and ICP analyses will be developed from a source independent of the standard solutions used for calibration. If the QA/QC value varies more than 5% from the accepted value, the batch will be reanalyzed.

A spike analysis will be included in each batch of IC and ICP analyses. In the IC analyses, a 10 mg/L nitrate spike will be analyzed. For the ICP analyses of the ammonium acetate extractable bases, a 10 mg/L magnesium spike will be analyzed. Any batch, for which the spike falls outside a 5% error range, will be reanalyzed.

An internal audit sample will be included in each batch of samples for each analytical procedure. This audit sample will be characterized for each analysis with 5 replications, prior to any batch analyses. An average of these replicates will be calculated and an error margin of 5% used to determine analytical failure or success. Any batch, for which the audit sample falls outside the 5% range, will be reanalyzed.

Analyses for all parameters will include a reagent blank to determine background levels and potential reagent or solvent contamination. Blanks will be analyzed under the same conditions as the samples.

All analyses performed on the IC and ICP will require standard curves of concentration versus conductance or millivolt, respectively. These calibration curves will be kept on file with the analyses.

## **12.0 PERFORMANCE AND SYSTEM AUDITS**

A systems audit by LADEQ would be welcome during the first quarter of field operations. Blind samples for audit purposes may be submitted by LADEQ to the Agronomy Department at any time in which analyses are in progress. All QA/QC issues will be reviewed with the project Quality Assurance Manager, Dr. E.P. Dunigan, on a monthly basis.

### **Field**

Field operation of equipment will be monitored for correct operating procedures and for safety. Use of the gasoline-powered generator for the electric pump requires routine maintenance to assure proper performance. Operation of equipment in an unacceptable or unsafe manner will be documented in writing in the sample log book and corrective action taken.

Sampling technique will be monitored to insure that wells are correctly pumped before samples are collected and that sample integrity is maintained during the collection process. Failure to follow established protocol will be documented in writing in the sample log book and corrective action taken.

Sample completeness will be monitored by checking the field log book against the samples collected per sampling event. Any missing samples will be identified and collected.

### **Laboratory**

Internal audit samples, spike samples, calibration checks, and independent QA/QC samples (defined above) will be monitored on a weekly basis so that corrective action can be taken in a timely fashion to optimize sample integrity. Any batch of samples identified as failing any of the above mentioned analytical checks will be documented and scheduled for reanalysis. If the problem persists, instrument operating conditions and sample preparation, among other possibilities, will be investigated.

## **13.0 PREVENTIVE MAINTENANCE**

Preventive maintenance for field equipment will include monitoring of lubricant fluid levels during operation of the gasoline-powered field generator which supplies current to the portable, submersible pump. Additional maintenance will be required to maintain the integrity of the monitoring wells when open and when buried. Sampling crews will be informed in the care, operation, and storage necessary for this equipment. A second submersible pump will not be kept in reserve due to its high cost. However, a replacement if needed, can be obtained locally.

Laboratory equipment will be serviced according to manufacturer specifications (Table 3).

## **14.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS**

Acceptable QA limits, as a percentage of standard deviation, are given by *Standard Methods* (APHA, 1989). Comparison with these limits will allow the project leader to detect deviations. Values in question will be reviewed and rerun where necessary to ascertain reliability.

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## **15.0 CORRECTIVE ACTION**

Laboratory corrective action will be the responsibility of the project leader. Close attention to, and occasional spot-checks, will be made to assure that (1) samples are correctly labeled, logged and transferred, (2) appropriate analyses are conducted, (3) instrument maintenance and reliability is satisfactory, (4) standard curves are correctly prepared and applied, and (5) calculations and significant figures used to quantify a sample are correctly applied. Attention to detail should eliminate most sources of error, however, unacceptable or suspect parameters will be re-analyzed.

## **16.0 QUALITY ASSURANCE REPORTS**

Field operations will be monitored for QA/QC matters and documented in the daily log book if unacceptable with the corrective action taken. All problems will be directed to the attention of the principal investigator.

Analytical QA/QC will be handled by the instrument operator where calibration of the instrument is concerned. Any problems will be entered into the sample log book. Any operational problems will be discussed with the principal investigator so that corrective action can be taken in as timely a manner as possible. Monitoring of spike samples, internal audit samples, and independent QA/QC samples will be monitored and documented on a weekly basis by the data compiler (principal investigator). Laboratories will be monitored for cleanliness and staff checked for using sound laboratory technique on a weekly basis.

The principal investigator will be responsible for monitoring, identifying and taking corrective action when needed, and reporting QA/QC matters. Each quarterly report submitted to LDEQ for the project will include a section addressing QA/QC matters. Any items failing to meet QA/QC standards will be reported along with the corrective action taken.

## 17.0

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# QUALITY ASSURANCE PROJECT PLAN

Seasonal Transport of Nitrate Into and Within a Groundwater Aquifer

LDEQ Interagency Agreement No.

## CONTRACTOR: LSU Agricultural Center, Agricultural Experimental Station

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Title: Project Manager

Signature and Date: Mark Walthall 6/19/95

Name: Dr. E. P. Dunigan

Title: Quality Assurance Officer

Signature and Date: E. P. Dunigan 6/19/95

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# QUALITY ASSURANCE PROJECT PLAN

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**SEASONAL TRANSPORT OF NITRATE  
INTO AND WITHIN A GROUND WATER AQUIFER  
QUALITY ASSURANCE AND QUALITY CONTROL  
FOR FIELD AND LABORATORY OPERATIONS**

**Principal Investigator  
P.M. Walthall  
Agronomy Department  
Louisiana Agricultural Experiment Station  
Louisiana State University Agricultural Center**

**Submitted to:  
Louisiana Department of Environmental Quality**

**November 1994**

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### 3.0 PROJECT DESCRIPTION

The purpose of this work is to show that nitrate levels which exceed health standards for drinking water (10 mg/L NO<sub>3</sub>-N) in a shallow ground water aquifer on the Macon Ridge in northeast Louisiana, are not random occurrences but can be predicted on a seasonal basis. Describing nitrate movement on a seasonal basis will be divided into two parts. **Objective 1** will focus specifically on transporting nitrate from the soil surface into the aquifer. **Objective 2** will describe dynamics within the aquifer which either concentrate nitrate at the top of the aquifer or disperse nitrate through lateral and/or vertical mixing.

We further propose to show that specific management practices can be used to effectively reduce nitrate levels over an annual cycle to meet health standards. **Objective 3** will demonstrate the effectiveness of specific management practices in regulating factors or processes which determine the amount of nitrate leached.

#### Objective 1

The strategy of this objective is to link soil and climatic factors which affect the mobility of nitrate to the variable concentrations of nitrate observed in the aquifer. The computer simulation model NLEAP (Nitrate Leaching and Economic Analysis Package), (Schafer, et al., 1991) will be used for modelling nitrate movement from the soil surface to the aquifer. The relevance of simulating the nitrate leaching process is to identify key factors or variables which can be manipulated by management practices to minimize nitrate leaching.

**Calibration** of the NLEAP model will be carried out during the early part of the study. A prerequisite for calibration of the model is that parameters necessary for model predictions be independently measured. It is planned to determine these parameters directly from soil measurements. If direct measurements are not experimentally feasible, estimates of such parameters specific to the soil series identified at our site will be used. This model contains regional soil and climate data bases containing data of specific soil properties for established soil series and local climate conditions. The soil data base consists of SCS soil characterization data of specific soil series.

Model input parameters include:

**Soil series** - The Gigger soil series is a very extensive soil type on the Macon Ridge and is recognized at our study site. The USDA-SCS taxonomic classification of the Gigger series is: fine-silty, mixed, thermic Typic Fragiudalf.

**Soil properties** - Two depth increments are recognized by the model for soil properties: 0 to 1 feet and 1 to 5 feet. Specific soil properties which will be determined for the Gigger soil at our site include: initial soil nitrate, organic carbon content, pH, CEC (exchangeable bases + exchangeable acidity). The model also

requires definition of an initial nitrate value for the deep vadose zone (between a depth of 5 feet and the top of the aquifer). Soil properties to be used from the Gigger soil data base will include: bulk density, water holding capacity and soil water content at 15 bars.

**Climate** - In the case of precipitation, daily measurements are recorded at the Macon Ridge Branch Experiment Station and will be used for an event by event analysis. Temperature readings needed to drive evapotranspiration will be obtained from the regional data base, using the St. Joseph climate data base, located approximately 40 miles east of our site.

**Validation** of the model for this phase of the study will address the amount of nitrate leached from the soil column (from the soil surface to the top of the aquifer). Linear regression will be used to examine how well predicted levels of nitrate leached by the model compare to actual nitrate levels observed in the soil column. The observed nitrate from soil columns will come from an existing data base collected over a three year period at the Macon Ridge Station in an adjacent field.

## **Objective 2**

While Objective 1 focuses on variables affecting nitrate movement over an annual cycle in the unsaturated zone (the soil column), **Objective 2** will focus on a different set of variables controlling movement within the aquifer. Some of these variables may follow an annual cycle and some may not. Two of the major variables we will attempt to characterize will be the variation in hydraulic gradient and hydraulic conductivity of the aquifer. These variables are important because of their influence on lateral dispersion which could play a major role in reducing concentrated nitrate plumes entering the aquifer. The hydraulic gradient will be determined by measuring water table elevations in three observation wells within a half mile radius of the study site. Hydraulic conductivity will be determined using a pressure transducer to measure the response of the aquifer to addition or withdrawal of a known slug. Hydraulic gradient and hydraulic conductivity measurements will be determined on a seasonal basis in which high and low river stage is considered as well as high and low rates of evapotranspiration.

Another variable which may affect aquifer dynamics at our site is the salinity gradient within the aquifer which results from the fresh water zone enriched with nitrate overlying a saline zone. While the approach will be somewhat empirical, it is critical to know the manner in which nitrate is dispersed either laterally or vertically. The NLEAP model recognizes an aquifer mixing zone varying in thickness from 1 to 10 feet and considers nitrate inputs as well as dilution from above and laterally. It is likely that simple dilution from leachate low in nitrate may account for reduction of elevated nitrate concentrations over an annual cycle, however, it is important to verify whether dispersion is actually confined to dilution

in the 10-foot mixing volume. To address this question we will use an  $\delta^{18}\text{O}$  stable isotope tracer to determine the contribution of both lateral and vertical dispersion (Gonthier and Aharon, 1990). The  $\delta^{18}\text{O}$  isotope is harmless regarding human health and will not contaminate the aquifer. This stable isotope also offers the advantage of not having to use a tracer such as bromide which can have density problems when introduced in high concentrations. Furthermore, this isotope has no adsorption characteristics common to some of the organic tracers in use. Monitoring wells have been configured such that a central 30-foot well will be spiked with the stable isotope, and the direction of flow detected either laterally by surrounding 30-, 40- and 50-foot wells located at a radius of 15 feet, or vertically by adjacent 40- and 50-foot wells. Sample collection for the tracer study will be on a scale of hours initially and reduced accordingly, dependent on conductivity.

### Objective 3

Two management practices will be evaluated for their effectiveness in regulating factors or processes which determine the amount of nitrate leached. The use of a split application of fertilizer will be tested for its ability to reduce the amount of nitrate available for leaching during the early part of the growing season. Preliminary work has shown that a critical time for leaching nitrate occurs between the time of planting and the establishment of the crop to the extent that evapotranspiration reduces effective leaching (usually the months of May and June). Approximately 45 kg/ha (50 lbs/ac) of ammonium nitrate will be applied at the time of planting in early May with a similar amount applied in early July. In the second growing season of the study a single application of nitrate will be used.

The use of a winter cover crop of wheat will be tested for its effectiveness in immobilizing residual nitrate over the winter season when evapotranspiration is at a minimum (in a bare field) and leaching potential is at a maximum. The winter cover crop will follow the split fertilizer application treatment. The second winter season following the one-time fertilizer application will use no winter cover crop.

Sample collection frequency for monitoring nitrate over an annual cycle will vary. Samples for monitoring nitrate levels will be collected weekly during critical periods: the first month after fertilizer applications and the first month after defoliation. Sampling will be adjusted to bi-weekly and monthly intervals during periods in which little change is likely to occur.

Linear regression will be used to examine the accuracy of the NLEAP model at this final stage, by comparing predicted aquifer nitrate levels to observed nitrate levels in monitoring wells. The results of the  $\delta^{18}\text{O}$  isotope tracer investigation will allow us to correct for any vertical dispersion effects otherwise not accounted for by the model.

## Time-Line for Field Activities.

### First Year

- January - Initiate bi-weekly sampling of monitoring wells.
- February - Install two additional wells for determining hydraulic gradient. Continue bi-weekly sampling of monitoring wells.
- April - Submerge monitoring wells. Collect soil cores for determining initial soil parameters.
- May - Plant cotton, apply first half of fertilizer amendment (45 kg/ha).
- June - Cultivate, open monitoring wells, initiate weekly (at least 4 weeks) sampling of wells for nitrate.
- July - Apply second half of fertilizer amendment (45 kg/ha), continue weekly (at least 4 weeks) sampling of wells for nitrate.
- August - Reduce sampling intensity of wells for nitrate to bi-weekly.
- September - Apply defoliant, harvest, increase sampling intensity for nitrates to weekly (at least 4 weeks).
- October - Collect soil cores for determining nitrate content of soil and vadose zone. Plant winter cover crop, reduce sampling intensity of wells for nitrate to bi-weekly.
- November - Continue bi-weekly sampling of monitoring wells for nitrate.
- December - Continue bi-weekly sampling of monitoring wells for nitrate.

### Second Year

- January - Continue bi-weekly sampling of monitoring wells for nitrate.
- February - Determine hydraulic conductivity and hydraulic gradient. Initiate first  $\delta^{18}\text{O}$  spike test (sampling strategy will be determined from hydraulic conductivity and gradient measurements). Continue bi-weekly sampling of monitoring wells for nitrate.
- March - Continue bi-weekly sampling of monitoring wells for nitrate.
- April - Continue bi-weekly sampling of monitoring wells for nitrate. Submerge monitoring wells, disk winter cover crop. Collect soil cores for determining nitrate content of soil and vadose zone.
- May - Plant cotton, apply single fertilizer amendment (90 kg/ha).
- June - Cultivate, open monitoring wells, initiate weekly (at least 4 weeks) sampling of wells for nitrate.
- July - Reduce sampling intensity of wells for nitrate to bi-weekly.
- August - Determine hydraulic conductivity and hydraulic gradient. Initiate second  $\delta^{18}\text{O}$  spike test. Continue bi-weekly sampling of monitoring wells for nitrate.
- September - Apply defoliant, harvest, increase sampling intensity for nitrates to weekly (at least 4 weeks).

- October - Collect soil cores for determining nitrate content of soil and vadose zone. Reduce sampling intensity of wells for nitrate to bi-weekly.
- November - Continue bi-weekly sampling of monitoring wells for nitrate.
- December - Continue bi-weekly sampling of monitoring wells for nitrate.

### Third Year

- January - Continue bi-weekly sampling of monitoring wells for nitrate.
- February - Continue bi-weekly sampling of monitoring wells for nitrate.
- March - Final sampling of monitoring wells for this study.

### Time-Line for Laboratory Activities.

#### First Year

(Nitrate analysis of well samples will be performed after each sampling event.

- January - Initiate calibration of NLEAP model.
- March - Quarterly Report
- April - Analyze soil samples for characterization of model parameters.
- June - Quarterly Report
- September - Quarterly Report
- November - Verification of nitrate leaching component of NLEAP using soil core data base.
- December - Annual Report.

#### Second Year

- January - Verification of aquifer response to use of split fertilizer application.
- February -  $\delta^{18}\text{O}$  isotope analysis from first spike test.
- March - Quarterly Report
- May - Verification of aquifer response to use of a winter cover crop.
- June - Quarterly Report
- August -  $\delta^{18}\text{O}$  isotope analysis from second spike test.
- September - Quarterly Report
- December - Annual Report.

#### Third Year

- January - Verification of aquifer response to use of single fertilizer application.



|             |   |
|-------------|---|
| March -     | Quarterly Report  |
| April -     | Laboratory analyses complete.   |
| May -       | Data compilation complete.  |
| June -      | Quarterly Report  |
| July -      | Verification of aquifer response to the absence of a winter cover crop. |
| September - | Quarterly Report  |
| October -   | Preparation of Final Report.  |
| December -  | Final Report.   |

#### **Intended Use of Acquired Data.**

The data acquired in this project will be used to demonstrate whether the management practices of using a split-application of fertilizer and a winter cover crop can effectively reduce excessive nitrate levels in ground water. The nitrate data base acquired from the monitoring wells will allow for verification of the NLEAP model. The  $\delta^{18}\text{O}$  data base will be used to identify any unexpected flow patterns in the aquifer that will need to be recognized if present. The purpose for this verification effort is to provide a calibrated management tool to producers of this region that is capable of evaluating a range of management schemes on crop yield and ground water quality.

#### **4.0 PROJECT ORGANIZATION AND RESPONSIBILITY**

Key individuals responsible for ensuring the collection of valid measurement data and the routine assessment of measurement systems for precision and accuracy are identified in Table 1.

#### **5.0 QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY**

Methodology used for the various chemical analyses is summarized in Table 2. The parameters have been discussed in **SECTION 3.0**. Cations will be analyzed by inductively coupled plasma spectrometry (ICP) and anions by ion chromatography (IC).

#### **6.0 SAMPLING PROCEDURES**

Sample collection will address three major tasks: (1) soil samples for calibrating the NLEAP model, (2) ground water samples for verifying nitrate leaching estimates from NLEAP, and (3) ground water samples for determining flow direction in the aquifer ( $\delta^{18}\text{O}$  isotope study). Sampling procedures will follow the recommendations in *Standard Methods* (APHA, 1989) where applicable.

**Soil Samples** will be collected using a Gidding's hydraulic probe. Cores, 2 inches in diameter, will be collected from three depth zones defined by the NLEAP model: 0 to 1 feet, 1 to 5 feet, and a deep vadose zone which will extend from 5 feet to the beginning of coarse aquifer sands, approximately 15 feet. Three replicate cores will be collected. All core holes will be back-filled with bentonite pellets. Soil samples will be sealed in plastic zip-lock bags for transport to the laboratory. Upon arrival to the laboratory at LSU, samples will be air-dried, ground if necessary to pass through a 2-mm sieve and stored until time of analyses.

**Water Samples** for both nitrate and isotope analyses will be collected using a Grundfos Redi-Flo2 portable, submersible pump. Each monitoring well will be purged of three well volumes as per USGS guidelines. Samples will be collected in acid-washed polyethylene bottles. Nitrate samples will be stored in ice chests during transport to the laboratory and refrigerated at 4° C prior to being analyzed. Samples will be scheduled for nitrate analysis within 48 hours of reaching the laboratory. Isotope samples will be transported to the laboratory under ambient conditions, sealed with parafilm and stored at room temperature in closed cabinets until time of analysis. These special precautions are to minimize any evaporation loss which would preferentially concentrate the  $\delta^{18}\text{O}$  isotope relative to the  $\delta^{16}\text{O}$  isotope. The ratio of these two isotopes is the critical factor in this analysis.

## **7.0 SAMPLE CUSTODY**

**Field Operations** - Water samples will be labeled with time, date, well number, and whether they are nitrate or  $\delta^{18}\text{O}$  isotope samples. Soil samples will be labeled with date and depth increment sampled from. Both soil and water samples will be logged into a field notebook at time of collection. Samples will be transported from the Macon Ridge Research Station to the LSU Agronomy Department on the day of sample collection for nitrates. Samples collected for the  $\delta^{18}\text{O}$  tracer study will be collected over a 2 to 3 day period before transport to the laboratory because of sampling intensity. During this time samples will be refrigerated at 4° C at the Macon Ridge Research Station.

**Laboratory Operations** - Upon delivery to the LSU Agronomy Department, samples will be logged into a laboratory notebook and double checked against the field notebook. Laboratory personnel will sign and date the log book to document arrival of samples.

All soil analyses will be completed in the LSU Agronomy Department. Nitrate analyses on well samples will be performed in the LSU Agronomy Department. The  $\delta^{18}\text{O}$  samples will be analyzed in the LSU Geology Department.

When a sample is analyzed, the sample number and type of analysis will be recorded in the log book. A hard copy printout of all analyses will be kept on file. Data will be stored on computer disks for analysis.

## **8.0 CALIBRATION PROCEDURES AND FREQUENCY**

**Field Equipment** - No field equipment involved in data acquisition requires calibration.

**Laboratory Equipment** - Table 3 lists the calibration procedures, frequencies, and tolerances for the equipment used for analyses of the proposed parameters.

## **9.0 ANALYTICAL PROCEDURES**

Analytical procedures were discussed under sections 3.0, 5.0, and 8.0.

## **10.0 DATA REDUCTION, VALIDATION AND REPORTING**

The lab analyst will perform the calculations and calibrations to quantify the concentration of a specific parameter. The data will then be transferred to a final data sheet and submitted to the project leader. Verification of calculations and transcriptions will be made by the project leader.

## **11.0 QUALITY CONTROL SAMPLE ANALYSES**

Appropriate standards (if available) from NBS or EPA will be run with each batch of samples.

Analyses for all parameters will include a reagent blank to determine background levels and potential reagent or solvent contamination. Blanks will be analyzed under the same conditions as the samples.

All analyses performed on the IC and ICP will require standard curves of concentration versus conductance or millivolt, respectively. These calibration curves will be kept on file with the analyses.

## **12.0 PERFORMANCE AND SYSTEM AUDITS**

A systems audit by LADEQ would be welcome during the first quarter of field operations. Blind samples for audit purposes may be submitted by LADEQ to the Agronomy Department at any time in which analyses are in progress.

### **13.0 PREVENTIVE MAINTENANCE**

Preventive maintenance for field equipment will include monitoring of lubricant fluid levels during operation of the gasoline-powered field generator which supplies current to the portable, submersible pump. Additional maintenance will be required to maintain the integrity of the monitoring wells when open and when buried. Sampling crews will be informed in the care, operation, and storage necessary for this equipment. A second submersible pump will not be kept in reserve due to its high cost. However, a replacement if needed, can be obtained locally.

Laboratory equipment will be serviced according to manufacturer specifications (Table 3).

### **14.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS**

Acceptable QA limits, as a percentage of standard deviation, are given by *Standard Methods* (APHA, 1989). Comparison with these limits will allow the project leader to detect deviations. Values in question will be reviewed and rerun where necessary to ascertain reliability.

### **15.0 CORRECTIVE ACTION**

Laboratory corrective action will be the responsibility of the project leader. Close attention to, and occasional spot-checks, will be made to assure that (1) samples are correctly labeled, logged and transferred, (2) appropriate analyses are conducted, (3) instrument maintenance and reliability is satisfactory, (4) standard curves are correctly prepared and applied, and (5) calculations and significant figures used to quantify a sample are correctly applied. Attention to detail should eliminate most sources of error, however, unacceptable or suspect parameters will be re-analyzed.

### **16.0 QUALITY ASSURANCE REPORTS**

Each instrument analyst will perform routine QA analyses previously described. These QA analyses will be monitored by the project leader for determining accuracy, precision, and representativeness.

**Table 1. Personnel and responsibility for the project.**

| Personnel  | Responsibility  |
|--|---|
| Dr. P.M. Walthall<br>Associate Professor<br>Department of Agronomy<br>Louisiana Agricultural Exp. Stn. | Overall Project Leader<br>Well Maintenance, Sample Collection,<br>Laboratory Analyses, Computer<br>Analyses |
| Dr. R.L. Hutchinson<br>Professor<br>Macon Ridge Research Station<br>Louisiana Agricultural Exp. Stn.   | On-Site Management<br>Planting, Fertilizing, Cultivating<br>Harvesting                                      |
| Dr. Paul Aharon<br>Professor<br>Dept. of Geology and Geophysics<br>Louisiana State University          | Supervision of $\delta^{18}\text{O}$ isotope analysis   |
| Ms. Joanie Haigler<br>Research Associate<br>Department of Agronomy<br>Louisiana Agricultural Exp. Stn. | Exchangeable Base Cations - ICP   |
| Ms. Lois West<br>Research Associate<br>Department of Agronomy<br>Louisiana Agricultural Exp. Stn.      | Nitrate Analysis - Ion Chromatography   |

**Table 2. Method of analysis for chemical and physical parameters.**

| Parameter                                       | Method/<br>Instrumentation   | Detection Limit   |
|---|--|---|
| Nitrate   | Dionex Ion Chromatograph<br>EPA Method 200.7   | 0.05 mg/L   |
| $\delta^{18}\text{O}$                           | Mass Spectrometer  | 0.1 ppt vs. SMOW†   |
| Organic Carbon<br>in Soil                       | Wet oxidation - titration  | 1.0 g/kg  |
| Soil pH   | Orion specific ion electrode   | 0.1 (pH units)  |
| Exchangeable<br>Base Cations<br>(Ca, Mg, Na, K) | Ammonium Acetate Extract<br>(Thomas, 1982)<br>Inductively Coupled Plasma<br>Spectrometer - EPA Method<br>200.7 | Ca 0.005 mg/L<br>Mg 0.02 mg/L<br>Na 0.03 mg/L<br>K 0.2 mg/L |
| Exchangeable<br>Acidity                         | Potassium Chloride Extract<br>Titration with 0.1 N NaOH<br>(Thomas, 1982)                                      | 0.5 meq/100g soil   |
| Hydraulic<br>Conductivity                       | Heath (1989)   |   |
| Hydraulic<br>Gradient                           | Heath (1989)   |   |

† Standard Mean Ocean Water

**Table 3. Calibration and tolerance of laboratory instruments.**

| Instrument         | Calibration and Tolerance |                                |
|--------------------|---------------------------|--------------------------------|
|                    | Time                      | Specifications                 |
| IC                 | Upon Use                  | NO <sub>3</sub> 0.2 to 40 mg/L |
| ICP                | Upon Use                  | Ca 0 to 250 mg/L               |
|                    |                           | Mg 0 to 250 mg/L               |
|                    |                           | Na 0 to 250 mg/L               |
|                    |                           | K 0 to 100 mg/L                |
| Mass Spectrometer  | Upon Use                  | -54 to -1 ppt vs. SMOW†        |
| pH Meter           | Upon Use                  | Buffers 4.0/7.0                |
| Analytical Balance | Monthly                   | 0.1 mg                         |

† Standard Mean Ocean Water

## 17.0

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